

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 26 OCT 2000

WIPO

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| Applicant's or agent's file reference 4566F/JAK | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) | |
| International application No. PCT/GB99/02501 | International filing date (day/month/year) 29/07/1999 | Priority date (day/month/year) 01/08/1998 |
| International Patent Classification (IPC) or national classification and IPC C03C17/245 | | |
| Applicant PILKINGTON PLC et al. | | |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

| | |
|---|--|
| Date of submission of the demand 18/01/2000 | Date of completion of this report 24.10.2000 |
| Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 | Authorized officer Somann, K Telephone No. +49 89 2399 8586  |

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/02501

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-6,8-11 as originally filed

7 as received on 04/10/2000 with letter of 28/09/2000

Claims, No.:

1-32 as received on 04/10/2000 with letter of 28/09/2000

Drawings, sheets:

1/2,2/2 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/02501

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | | | |
|-------------------------------|------|--------|----------|
| Novelty (N) | Yes: | Claims | 1-30, 32 |
| | No: | Claims | 31 |
| Inventive step (IS) | Yes: | Claims | 1-30 |
| | No: | Claims | 32 |
| Industrial applicability (IA) | Yes: | Claims | 1-32 |
| | No: | Claims | |

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02501

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1: DAI, GUORUI ET AL: 'A study of tungsten oxide thin films prepared by plasma enhanced CVD (PECVD)' ADV. SCI. TECHNOL. (1995), 5(ADVANCES IN INORGANIC FILMS AND COATINGS), 407-414 , XP002123373
- D2: CHEMICAL ABSTRACTS, vol. 126, no. 15, 14 April 1997 (1997-04-14) Columbus, Ohio, US; abstract no. 205647, HUI, BORAN ET AL: 'Tungsten oxide thin films prepared by using tungsten oxychloride as a precursor' XP002123375 & JILIN DAXUE ZIRAN KEXUE XUEBAO (1996), (3), 49-52 ,
- D3: DAVAZOGLU D ET AL: 'STRUCTURE AND OPTICAL PROPERTIES OF WO₃ THIN FILMS PREPARED BY CHEMICAL VAPOUR DEPOSITION' THIN SOLID FILMS MAR 2 1987, vol. 147, no. 2, 2 March 1987 (1987-03-02), pages 131-142, XP002123374
- D4: ENNAOUI A ET AL: 'Preparation of textured and photoactive 2H-WS₂ thin films by sulfurization of WO₃' THIN SOLID FILMS, vol. 261, no. 1/2, 1 June 1995 (1995-06-01), page 124-131 XP004003740 ISSN: 0040-6090
- D5: EP-A-0 546 669 (FORD WERKE AG ;FORD FRANCE (FR); FORD MOTOR CO (GB)) 16 June 1993 (1993-06-16) cited in the application
- D6: ROTHSCHILD M ET AL: 'EXCIMER-LASER-INDUCED SUB-0.5UM PATTERNING OF WO₃ THIN FILMS' APPLIED PHYSICS LETTERS, vol. 59, no. 14, 30 September 1991 (1991-09-30), pages 1790-1792, XP000250019 ISSN: 0003-6951

The subject-matter of Claims 1 to 19 and 27 to 29 is new with respect to the prior art cited in the search report by virtue of the feature, which defines the temperature at which the substrate is to be held during the claimed process as 500°C to 720°C.

The subject-matter of Claims 20 to 26 is new with respect to the prior art cited in the search report by virtue of the feature, which refers to the overcoating defined in the characterising portion of Claim 20.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02501

The subject-matter of Claim 30 is new with respect to the prior art cited in the search report by virtue of the feature which refers to an ester as a tone of the reagents in the gaseous stream directed to the surface of the glass substrate.

The subject-matter of product Claim 31 cannot be distinguished on the basis of this feature from the products prepared by the processes according to the prior art of any of D1 to D6. Consequently the product according to this Claim is indistinguishable from those known in the prior art.

There is no prior art available mentioning multiple glazing units of the nature defined in Claim 32 in connection with the coated glass recited in Claim 31. The subject-matter of Claim 32 is therefore new with respect to the cited prior art. Document D5, however, mentions in line 58 on page 2 to line 1 of page 3 and in lines 29 to 32 on page 3 architectural glazing manufactured using a process for applying a film which results in a coated glass indistinguishable from that claimed in Claim 31. The skilled person would regard it as obvious to apply the prior art disclosed in D5 to glazings which are also multiple glazings, since in most temperate to cold climate countries multiple glazing is the usual form of glazing.

The subject-matter of Claims 1 to 30 is inventive with respect to the available prior art, since any of the distinguishing features discussed above lead either to a faster deposition rate (at least 2.7 nm/sec - see results in appropriate column of Table I) or a more durable tungsten oxide coating. None of the available prior art suggest to the person skilled in the art making use of any of the besaid distinguishing features to solve the problem of improvements in durability or enhancements in deposition rates for coatings as claimed by the invention.

A nitrogen carrier gas feed was passed through a bubbler (corresponding to bubbler 2 in Figure 1) maintained at a temperature of 30°C at a flow rate of 1 litre/min, the bubbler containing either ethyl or butyl acetate. A separate nitrogen carrier gas feed was passed over solid WOCl_4 in a standard bubbler (bubbler 1), the bubbler situated in an oven 8 to maintain the precursor in a temperature range 170 - 185°C. Thermal decomposition of WOCl_4 is low and good precursor transport and growth was still achieved after 20 hours in this temperature range. The separate carrier gas feeds, one with entrained ester and the other with entrained WOCl_4 , were combined to form a precursor gas mixture. A nitrogen make-up of 5.5 litres/min and oxygen gas were added to dilute the precursor gas mixture and the diluted precursor gas mixture was delivered through a line (20) to the reactor, the line maintained at a temperature of 200°C. The diluted precursor gas mixture was directed on to the heated glass substrate in the reactor resulting in the deposition of a tungsten oxide coating. The deposition process was continued for a run time of 10 or 30 seconds. At the end of the deposition process, the coated glass was allowed to cool to room temperature under nitrogen. The thickness of the tungsten oxide coating was measured by standard optical (optical constants were obtained from the spectra and the spectra modelled to determine the larger thicknesses) and/or stylus methods. Similar methods were used to measure all layer thicknesses in the Examples.

Table 1 shows the ester used in each Example together with the flow rate of oxygen added to the precursor gas mixture, the run time of the coating process, the thickness of tungsten oxide deposited and the peak growth rate (growth rate of the thickest part of the layer) of the tungsten oxide coating. It was observed that for constant ethyl acetate concentration, growth rate dropped with increasing oxygen concentration.

Bubbler 1 was fitted with a 100 pound per square inch (0.69 MPa) pressure relief valve to minimise risk from over-pressurisation, which could occur, for example, if there were any blockage of the bubbler or delivery lines. Particular care was taken to exclude moisture from the delivery lines and WOCl_4 bubbler because the precursor appears to have an increased sensitivity to moisture at elevated temperature.

The coating process appeared to be affected significantly by substrate temperature. During preparation and performance of these Examples the best deposition temperature range appeared to be 565 - 655°C.

CLAIMS

1. A process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and a source of oxygen on to the surface of the glass substrate, characterised in that the glass substrate is at a temperature in the range 500°C to 720°C.
2. A process according to claim 1 wherein the coating comprising tungsten oxide comprises a layer of tungsten oxide.
3. A process according to claim 1 or claim 2 wherein tungsten oxyhalide comprises a tungsten oxychloride, preferably tungsten oxytetrachloride.
4. A process according to any preceding claim wherein tungsten oxyhalide or tungsten chloride comprises a substituted tungsten oxyhalide or tungsten chloride.
5. A process according to any preceding claim wherein the source of oxygen comprises an ester.
6. A process according to claim 5 wherein the ester has from 3 to 6 carbon atoms.
7. A process according to claim 5 or 6 wherein the ester is ethyl acetate or butyl acetate.
8. A process according to any preceding claim wherein the gaseous stream contains oxygen gas.
9. A process according to any preceding claim wherein the ratio of tungsten oxyhalide or tungsten chloride and the source of oxygen are such that the layer of tungsten oxide is deposited as non-stoichiometric tungsten oxide.

10. A process according to any preceding claim wherein the gaseous stream contains a source of fluorine.
11. A process according to claim 10 wherein the source of fluorine comprises hexafluoroethane, trifluoroacetic acid or hexafluoropropylene oxide.
12. A process according to any preceding claim wherein tungsten oxyhalide or tungsten chloride is entrained in the gaseous stream by flowing inert gas over hot tungsten oxyhalide or tungsten chloride.
13. A process according to claim 12 wherein tungsten oxyhalide or tungsten chloride is at a temperature in the range 170°C to 210°C.
14. A process according to claim 12 or 13 wherein the inert gas comprises nitrogen.
15. A process according to any preceding claim wherein the source of oxygen comprises an ester and is entrained in the gaseous stream by contacting said ester with a flowing inert gas.
16. A process according to claim 15 wherein the ester is at a temperature in the range 30°C to 45°C.
17. A process according to any preceding claim wherein the tungsten oxide layer has a thickness in the range 70 to 180 nm.
18. A process according to any preceding claim wherein the tungsten oxide layer is deposited at a growth rate in the range 3 to 25 nm s⁻¹.
19. A process according to any preceding claim wherein the tungsten oxide layer is overcoated with a further layer.

20. A process for coating glass comprising directing a gaseous stream containing a tungsten compound and a source of oxygen on to the surface of a glass substrate thereby forming a non-stoichiometric tungsten oxide layer characterised in that the tungsten oxide layer is overcoated with a further layer.
21. A process according to claim 19 or 20 wherein the further layer comprises a metal oxide.
22. A process according to claims 19 to 21 wherein the further layer comprises fluorine doped tin oxide.
23. A process according to any preceding claim wherein the process is performed during the float glass production process.
24. A process according to any preceding claim wherein the glass substrate is at a temperature in the range 565°C to 655°C.
25. A process according to any preceding claim wherein the tungsten oxide layer is deposited on to coated glass.
26. A process according to claim 25 wherein the coated glass has a coating comprising silicon oxide, preferably containing carbon.
27. A process for coating glass comprising entraining a tungsten compound in a gas by flowing the gas over a tungsten compound at a temperature below its melting point and directing the gaseous stream on to the surface of a glass substrate thereby forming a tungsten oxide layer, characterised in that the glass substrate is at a temperature in the range 500°C to 720°C.
28. A process according to claim 27 wherein the tungsten compound is tungsten halide, tungsten oxyhalide or tungsten carbonyl.

29. A method of coating glass comprising
- (a) providing a glass substrate having a temperature in the range 500°C to 720°C,
 - (b) preparing a gaseous stream comprising a source of oxygen and a tungsten compound selected from the group consisting essentially of tungsten oxyhalide and tungsten chloride, and
 - (c) directing the gaseous stream on to the glass substrate, thereby depositing a coating comprising tungsten oxide on the glass substrate.
30. A process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and an ester on to the surface of the glass substrate.
31. A coated glass produced by a process according to any preceding claim.
32. A multiple glazing unit comprising a coated glass according to claim 31 in spaced opposed relation to a glazing pane.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



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| Applicant's or agent's file reference 4566F/JAK | | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
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| Date of submission of the demand 18/01/2000 | Date of completion of this report 24.10.2000 |
| Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 | Authorized officer Somann, K Telephone No. +49 89 2399 8586  |

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see separate sheet

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International application No. PCT/GB99/02501

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There is no prior art available mentioning multiple glazing units of the nature defined in Claim 32 in connection with the coated glass recited in Claim 31. The subject-matter of Claim 32 is therefore new with respect to the cited prior art. Document D5, however, mentions in line 58 on page 2 to line 1 of page 3 and in lines 29 to 32 on page 3 architectural glazing manufactured using a process for applying a film which results in a coated glass indistinguishable from that claimed in Claim 31. The skilled person would regard it as obvious to apply the prior art disclosed in D5 to glazings which are also multiple glazings, since in most temperate to cold climate countries multiple glazing is the usual form of glazing.

The subject-matter of Claims 1 to 30 is inventive with respect to the available prior art, since any of the distinguishing features discussed above lead either to a faster deposition rate (at least 2.7 nm/sec - see results in appropriate column of Table I) or a more durable tungsten oxide coating. None of the available prior art suggest to the person skilled in the art making use of any of the besaid distinguishing features to solve the problem of improvements in durability or enhancements in deposition rates for coatings as claimed by the invention.

INTERNATIONAL COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year)

15 March 2000 (15.03.00)

International application No.

PCT/GB99/02501

Applicant's or agent's file reference

4566F/JAK

International filing date (day/month/year)

29 July 1999 (29.07.99)

Priority date (day/month/year)

01 August 1998 (01.08.98)

Applicant

SANDERSON, Kevin, David

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

18 January 2000 (18.01.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Juan Cruz

Telephone No.: (41-22) 338.83.38

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/GB 99/02501

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C17/245 C03C17/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7. C03C.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------------|
| X | DAI, GUORUI ET AL: "A study of tungsten oxide thin films prepared by plasma enhanced CVD (PECVD)" ADV. SCI. TECHNOL. (1995), 5(ADVANCES IN INORGANIC FILMS AND COATINGS), 407-414 , XP002123373 the whole document -/- | 1-3,8,9, 12,26, 28-31 |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

19 November 1999

Date of mailing of the international search report

13/12/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Somann, K

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB.99/02501

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------------|
| X | CHEMICAL ABSTRACTS, vol. 126, no. 15, 14 April 1997 (1997-04-14) Columbus, Ohio, US; abstract no. 205647, HUI, BORAN ET AL: "Tungsten oxide thin films prepared by using tungsten oxychloride as a precursor" XP002123375 abstract & JILIN DAXUE ZIRAN KEXUE XUEBAO (1996), (3), 49-52 , ---- | 1-3,8,9, 12,26, 28-31 |
| X | DAVAZOGLU D ET AL: "STRUCTURE AND OPTICAL PROPERTIES OF WO3 THIN FILMS PREPARED BY CHEMICAL VAPOUR DEPOSITION" THIN SOLID FILMS MAR 2 1987, vol. 147, no. 2, 2 March 1987 (1987-03-02), pages 131-142, XP002123374 page 131, last line ---- | 28,29 |
| X | ENNAOUI A ET AL: "Preparation of textured and photoactive 2H-WS2 thin films by sulfurization of WO3" THIN SOLID FILMS, vol. 261, no. 1/2, 1 June 1995 (1995-06-01), page 124-131 XP004003740 ISSN: 0040-6090 "2. Experimental methods" page 125, left-hand column ---- | 28,29 |
| X | EP 0 546 669 A (FORD WERKE AG ;FORD FRANCE (FR); FORD MOTOR CO (GB)) 16 June 1993 (1993-06-16) cited in the application page 3, line 43 - line 47 ---- | 28 |
| X | ROTHSCHILD M ET AL: "EXCIMER-LASER-INDUCED SUB-0.5UM PATTERNING OF WO3 THIN FILMS" APPLIED PHYSICS LETTERS, vol. 59, no. 14, 30 September 1991 (1991-09-30), pages 1790-1792, XP000250019 ISSN: 0003-6951 page 1790, left-hand column, line 1, paragraph 2 - line 7, paragraph 2 ----- -/-- | 28 |

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02501

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | <p>CHEMICAL ABSTRACTS, vol. 116, no. 2, 13 January 1992 (1992-01-13) Columbus, Ohio, US; abstract no. 13556, JUDEINSTEIN, PATRICK ET AL: "Sol-Gel synthesis of tungsten trioxide thin films" XP002123376 abstract & J. MATER. CHEM. (1991), 1(4), 621-7 , -----</p> | 1-32 |

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No.

PCT/GB 99/02501

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 0546669 A | 16-06-1993 | US 5286520 A | 15-02-1994 |
| | | CA 2085025 A | 14-06-1993 |
| | | DE 69209988 D | 23-05-1996 |
| | | DE 69209988 T | 05-09-1996 |

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

| | | |
|---|---|--|
| Applicant's or agent's file reference 4566F/JAK | FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. | |
| International application No. PCT/GB 99/ 02501 | International filing date (day/month/year) 29/07/1999 | (Earliest) Priority Date (day/month/year) 01/08/1998 |
| Applicant PILKINGTON PLC et al. | | |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

National Application No.
PCT/GB 99/02501

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C17/245 C03C17/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|--------------------------------|
| X | DAI, GUORUI ET AL: "A study of tungsten oxide thin films prepared by plasma enhanced CVD (PECVD)" ADV. SCI. TECHNOL. (1995), 5(ADVANCES IN INORGANIC FILMS AND COATINGS), 407-414 , XP002123373 the whole document — —/— | 1-3, 8, 9, 12, 26, 28-31 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

19 November 1999

Date of mailing of the international search report

13/12/1999

Name and mailing address of the ISA

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Authorized officer

Somann, K

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/02501

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------------|
| X | CHEMICAL ABSTRACTS, vol. 126, no. 15, 14 April 1997 (1997-04-14) Columbus, Ohio, US; abstract no. 205647, HUI, BORAN ET AL: "Tungsten oxide thin films prepared by using tungsten oxychloride as a precursor" XP002123375 abstract & JILIN DAXUE ZIRAN KEXUE XUEBAO (1996), (3), 49-52 , | 1-3,8,9, 12,26, 28-31 |
| X | DAVAZOGLU D ET AL: "STRUCTURE AND OPTICAL PROPERTIES OF WO3 THIN FILMS PREPARED BY CHEMICAL VAPOUR DEPOSITION" THIN SOLID FILMS MAR 2 1987, vol. 147, no. 2, 2 March 1987 (1987-03-02), pages 131-142, XP002123374 page 131, last line | 28,29 |
| X | ENNAOUI A ET AL: "Preparation of textured and photoactive 2H-WS2 thin films by sulfurization of WO3" THIN SOLID FILMS, vol. 261, no. 1/2, 1 June 1995 (1995-06-01), page 124-131 XP004003740 ISSN: 0040-6090 "2. Experimental methods" page 125, left-hand column | 28,29 |
| X | EP 0 546 669 A (FORD WERKE AG ;FORD FRANCE (FR); FORD MOTOR CO (GB)) 16 June 1993 (1993-06-16) cited in the application page 3, line 43 - line 47 | 28 |
| X | ROTHSCHILD M ET AL: "EXCIMER-LASER-INDUCED SUB-0.5UM PATTERNING OF WO3 THIN FILMS" APPLIED PHYSICS LETTERS, vol. 59, no. 14, 30 September 1991 (1991-09-30), pages 1790-1792, XP000250019 ISSN: 0003-6951 page 1790, left-hand column, line 1, paragraph 2 - line 7, paragraph 2 | 28 |
| | -/- | |

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/02501

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | <p>CHEMICAL ABSTRACTS, vol. 116, no. 2, 13 January 1992 (1992-01-13) Columbus, Ohio, US; abstract no. 13556, JUDEINSTEIN, PATRICK ET AL: "Sol-Gel synthesis of tungsten trioxide thin films" XP002123376 abstract & J. MATER. CHEM. (1991), 1(4), 621-7 ,</p> | 1-32 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02501

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 0546669 A | 16-06-1993 | US 5286520 A | 15-02-1994 |
| | | CA 2085025 A | 14-06-1993 |
| | | DE 69209988 D | 23-05-1996 |
| | | DE 69209988 T | 05-09-1996 |

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500 Rec'd PCT/PTO 2 4 JAN 2001

PTO/SB/93 (10-96)

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FILING IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) UNDER 35 U.S.C. 371

Title: Process for Coating Glass

Inventor: Kevin David Sanderson

Int'l Appln: PCT/GB99/02501 filed 29 July 1999

Priority Date: 01 August 1998

Attorneys: Marshall & Melhorn, LLC

Docket No: 1-15240

09/744420

500 Rec'd PCT/PTO 24 JAN 2001

A nitrogen carrier gas feed was passed through a bubbler (corresponding to bubbler 2 in Figure 1) maintained at a temperature of 30°C at a flow rate of 1 litre/min, the bubbler containing either ethyl or butyl acetate. A separate nitrogen carrier gas feed was passed over solid WOCl_4 in a standard bubbler (bubbler 1), the bubbler situated in an oven 8 to maintain the precursor in a temperature range 170 - 185°C. Thermal decomposition of WOCl_4 is low and good precursor transport and growth was still achieved after 20 hours in this temperature range. The separate carrier gas feeds, one with entrained ester and the other with entrained WOCl_4 , were combined to form a precursor gas mixture. A nitrogen make-up of 5.5 litres/min and oxygen gas were added to dilute the precursor gas mixture and the diluted precursor gas mixture was delivered through a line (20) to the reactor, the line maintained at a temperature of 200°C. The diluted precursor gas mixture was directed on to the heated glass substrate in the reactor resulting in the deposition of a tungsten oxide coating. The deposition process was continued for a run time of 10 or 30 seconds. At the end of the deposition process, the coated glass was allowed to cool to room temperature under nitrogen. The thickness of the tungsten oxide coating was measured by standard optical (optical constants were obtained from the spectra and the spectra modelled to determine the larger thicknesses) and/or stylus methods. Similar methods were used to measure all layer thicknesses in the Examples.

Table 1 shows the ester used in each Example together with the flow rate of oxygen added to the precursor gas mixture, the run time of the coating process, the thickness of tungsten oxide deposited and the peak growth rate (growth rate of the thickest part of the layer) of the tungsten oxide coating. It was observed that for constant ethyl acetate concentration, growth rate dropped with increasing oxygen concentration.

Bubbler 1 was fitted with a 100 pound per square inch (0.69 MPa) pressure relief valve to minimise risk from over-pressurisation, which could occur, for example, if there were any blockage of the bubbler or delivery lines. Particular care was taken to exclude moisture from the delivery lines and WOCl_4 bubbler because the precursor appears to have an increased sensitivity to moisture at elevated temperature.

The coating process appeared to be affected significantly by substrate temperature. During preparation and performance of these Examples the best deposition temperature range appeared to be 565 - 655°C.

CLAIMS

1. A process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and a source of oxygen on to the surface of the glass substrate, characterised in that the glass substrate is at a temperature in the range 500°C to 720°C.
2. A process according to claim 1 wherein the coating comprising tungsten oxide comprises a layer of tungsten oxide.
3. A process according to claim 1 or claim 2 wherein tungsten oxyhalide comprises a tungsten oxychloride, preferably tungsten oxytetrachloride.
4. A process according to any preceding claim wherein tungsten oxyhalide or tungsten chloride comprises a substituted tungsten oxyhalide or tungsten chloride.
5. A process according to any preceding claim wherein the source of oxygen comprises an ester.
6. A process according to claim 5 wherein the ester has from 3 to 6 carbon atoms.
7. A process according to claim 5 or 6 wherein the ester is ethyl acetate or butyl acetate.
8. A process according to any preceding claim wherein the gaseous stream contains oxygen gas.
9. A process according to any preceding claim wherein the ratio of tungsten oxyhalide or tungsten chloride and the source of oxygen are such that the layer of tungsten oxide is deposited as non-stoichiometric tungsten oxide.

10. A process according to any preceding claim wherein the gaseous stream contains a source of fluorine.
11. A process according to claim 10 wherein the source of fluorine comprises hexafluoroethane, trifluoroacetic acid or hexafluoropropylene oxide.
12. A process according to any preceding claim wherein tungsten oxyhalide or tungsten chloride is entrained in the gaseous stream by flowing inert gas over hot tungsten oxyhalide or tungsten chloride.
13. A process according to claim 12 wherein tungsten oxyhalide or tungsten chloride is at a temperature in the range 170°C to 210°C.
14. A process according to claim 12 or 13 wherein the inert gas comprises nitrogen.
15. A process according to any preceding claim wherein the source of oxygen comprises an ester and is entrained in the gaseous stream by contacting said ester with a flowing inert gas.
16. A process according to claim 15 wherein the ester is at a temperature in the range 30°C to 45°C.
17. A process according to any preceding claim wherein the tungsten oxide layer has a thickness in the range 70 to 180 nm.
18. A process according to any preceding claim wherein the tungsten oxide layer is deposited at a growth rate in the range 3 to 25 nm s⁻¹.
19. A process according to any preceding claim wherein the tungsten oxide layer is overcoated with a further layer.

20. A process for coating glass comprising directing a gaseous stream containing a tungsten compound and a source of oxygen on to the surface of a glass substrate thereby forming a non-stoichiometric tungsten oxide layer characterised in that the tungsten oxide layer is overcoated with a further layer.
21. A process according to claim 19 or 20 wherein the further layer comprises a metal oxide.
22. A process according to claims 19 to 21 wherein the further layer comprises fluorine doped tin oxide.
23. A process according to any preceding claim wherein the process is performed during the float glass production process.
24. A process according to any preceding claim wherein the glass substrate is at a temperature in the range 565°C to 655°C.
25. A process according to any preceding claim wherein the tungsten oxide layer is deposited on to coated glass.
26. A process according to claim 25 wherein the coated glass has a coating comprising silicon oxide, preferably containing carbon.
27. A process for coating glass comprising entraining a tungsten compound in a gas by flowing the gas over a tungsten compound at a temperature below its melting point and directing the gaseous stream on to the surface of a glass substrate thereby forming a tungsten oxide layer, characterised in that the glass substrate is at a temperature in the range 500°C to 720°C.
28. A process according to claim 27 wherein the tungsten compound is tungsten halide, tungsten oxyhalide or tungsten carbonyl.

29. A method of coating glass comprising
- (a) providing a glass substrate having a temperature in the range 500°C to 720°C,
 - (b) preparing a gaseous stream comprising a source of oxygen and a tungsten compound selected from the group consisting essentially of tungsten oxyhalide and tungsten chloride, and
 - (c) directing the gaseous stream on to the glass substrate, thereby depositing a coating comprising tungsten oxide on the glass substrate.
30. A process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and an ester on to the surface of the glass substrate.
31. A coated glass produced by a process according to any preceding claim.
32. A multiple glazing unit comprising a coated glass according to claim 31 in spaced opposed relation to a glazing pane.